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Review

Metal segregation in bimetallic clusters and its possible role in synergism and bifunctional catalysis

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Abstract

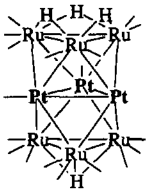
Aspects of the reactivity of segregated bimetallic compounds and their unusual catalytic properties are reviewed with an emphasis on the author's own studies of platinum–ruthenium mixed-metal cluster complexes and their ability to produce hydrogenation and hydrosilylation of alkynes, catalytically. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Catalysis; Bimetallic; Mixed-metal; Synergism; Platinum; Ruthenium

1. Introduction

Recent studies have provided numerous examples of high-nuclearity mixed-metal cluster complexes that exhibit segregation of the metal atoms within the cluster unit [1–4], e.g. $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu\text{-}H)_3$ (1) [1f] and $[Ni_{38}Pt_6CO)_{48}H_{6-n}]^{n-}$ (2) [2] and $[Cu_7Ru_8(CO)_{24}Cl_3H_2]^{2-}$ (3) [4].

It has now been demonstrated amply in the area of catalysis that many metal alloys, supported bimetallic clusters and bimetallic thin films exhibit catalytic properties that are significantly superior to those of the individual components [5,6]. In fact, today, highly dispersed supported bimetallic cluster catalysts of platinum mixed with rhenium or iridium are used widely and routinely by the petroleum industry in the process of petroleum reforming [5a]. These catalysts have higher activities and longer lifetimes than pure platinum and produce automotive fuels more efficiently with higher octane ratings and with fewer waste products. These advances have played a key role in the development and the production of the unleaded gasolines that are in use today [5a,b].



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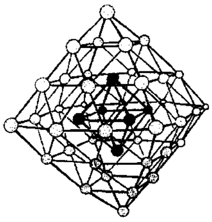

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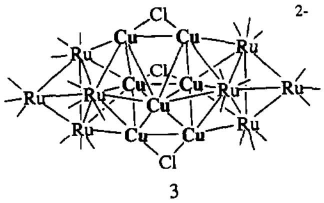

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Studies have shown that the highly dispersed heterogeneous bimetallic reforming catalysts and certain bi-

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nary mixtures of transition metals also exhibit a pronounced tendency to *segregate their elements* according to type [5,7]. These observations are supported by theoretical calculations [7c–f]. There is evidence for segregation of platinum and ruthenium on the surface of annealed platinum–ruthenium alloys and their particles [8]. These segregation processes result in the formation of microinterfaces between the two types of metal atoms. While it is believed widely that the more exposed 'step', 'kink' and 'adatom' sites exhibit the highest reactivity on the surfaces of pure metals [9], it seems unlikely that the reactivity at such homonuclear sites can explain fully the synergistic phenomena exhibited by segregated bimetallic cluster catalysts. Instead, it is likely that many of the syngeristic effects of highly dispersed bimetallic clusters may be traced to reactivity proximate to heteronuclear ensembles of metal atoms in the vicinity of these microinterfaces. Indeed, step, kink and adaatom sites in the proximity of these interfaces may prove to be among the more important reactivity sites.

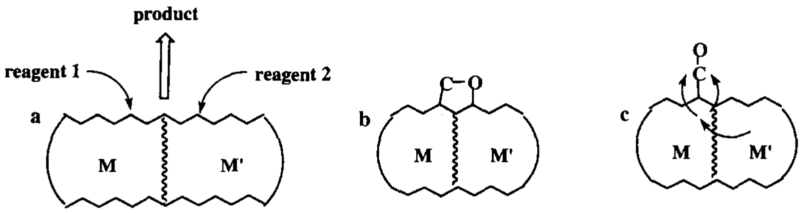
It has been shown that certain segregated copper–ruthenium catalysts have higher reactivities for some reactions than the pure metals [10]. It has been suggested that the two metals may catalyze different steps of the reaction cooperatively [10a]. In fact, the well-established phenomenon known as spillover (i.e. transfer of an activated species from an active surface across an interface to a second surface) observed in heterogeneous catalysis is based on this concept [11]. Segregated bimetallic thin films may be good models for highly dispersed segregated bimetallic cluster catalysts. Studies of bimetallic thin films have shown that one metal can cause significant electronic changes upon the other metal and in turn influence its ability to adsorb small molecules and perform catalysis [6,12]. Goodman and co-workers have elegantly shown that strained overlayers in bimetallic films exhibit enhanced reactivity, but an important question that remains is 'What is the character of the reactivity of unstrained, annealed real-world segregated bimetallic cluster catalysts functioning at the usual elevated reaction temperatures?' It has been suggested for some cases that metal atoms near the edges of islands on metal segregated bimetallic surfaces may exhibit higher reactivity than interior atoms [13]. Such edge atoms will be more reactive due to their lower coordination, but these atoms will also be more susceptible to the effects of bimetallic/interfacial phenomena.

Recent studies have shown that polynuclear metal cluster complexes are also capable of performing a variety of organic transformations catalytically [14], and there is evidence that certain mixed-metal cluster complexes do exhibit superior catalytic properties [15]. In an effort to understand the nature of the synergism in bimetallic reforming catalysts, interest in the chemistry of heteronuclear cluster complexes containing platinum has developed [16]. Muetterties, Yates and others have discussed the relationships between polynuclear metal complexes and surfaces and the role that metal cluster complexes could serve as models for heterogeneous catalysts [17]. This correlation is known as the 'cluster–surface analogy' and evidence supporting it continues to accumulate [17d,e].

It seems reasonable to extend this concept to mixed-metal cluster complexes [16d]. Segregated mixed-metal cluster complexes could, in some cases, serve as viable models for segregated heteronuclear heterogeneous catalysts, and their studies could provide information relating to the reactivity at metal–metal interfaces, particularly pertaining to mixed-metal ensembles. The number of examples of metal clusters as catalysts and catalyst precursors under homogeneous conditions continues to increase [14]. Cluster complexes deposited on supports also appear to have great potential as precursors for supported heterogeneous catalysts [10a,15].

A number of mechanisms for bimetallic activation of organic molecules in catalytic reactions have been discussed. Some of these are shown in Fig. 1. In all of these, the bimetallic interface is a central feature of the reactivity.

By one mechanism, one reagent is activated on one of the metals **M** and a second reagent is activated on the other **M′** (Fig. 1(a)). The activated reagents can migrate toward one another and then combine. This is analogous to the spillover phenomena observed for heterogeneous catalysts [11]. The product might be formed and released in the proximity of the bimetallic interface, although this is not a requirement. Studies of metal cluster complexes and metal surfaces have shown



bimetallic cluster

multisite activation

A metal to metal "ligand" effect

Fig. 1.

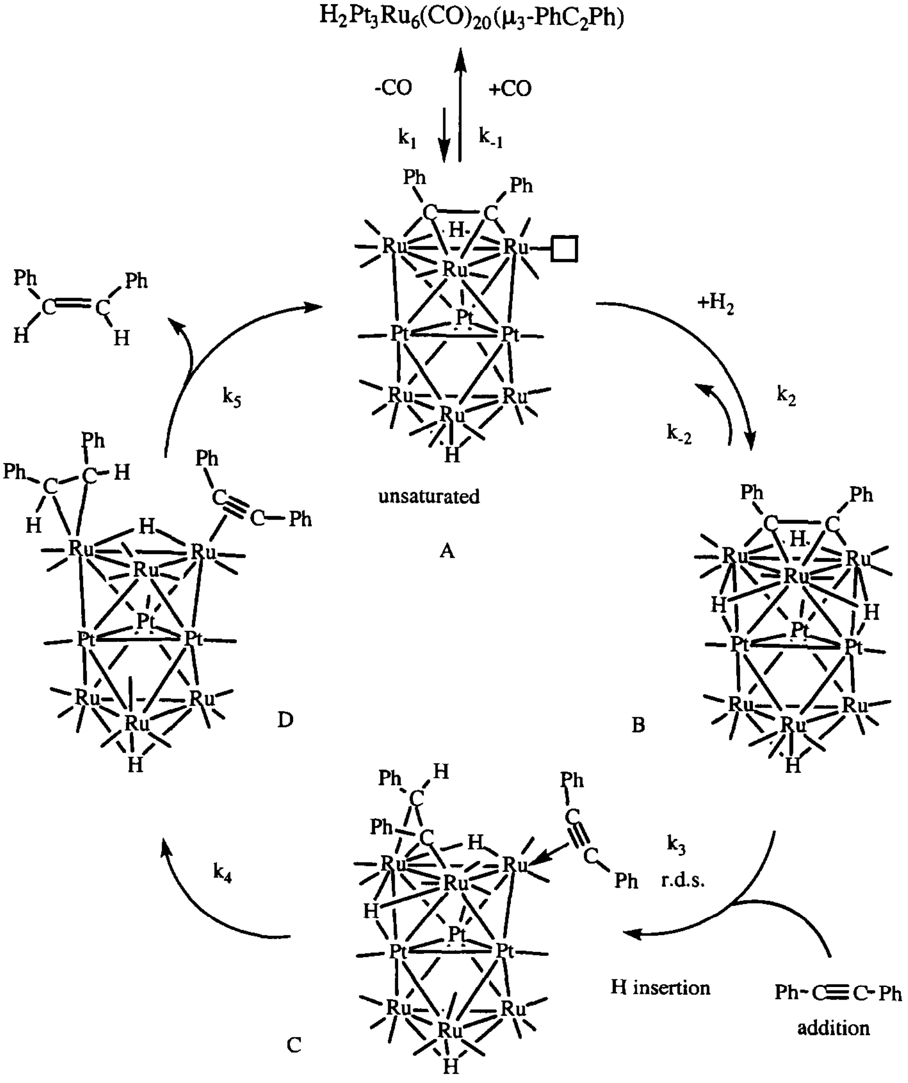
that many types of ligands, such as hydrides, CO, alkynes and alkenyl groups are able to move readily from one metal atom to another [11,17a].

A second mechanism, multi-site activation, that has been proposed to explain some of the superior properties of certain bimetallic supported catalysts to produce activation of CO, must occur at the interface (see Fig. 1(b)). In this case, the bimetallic ensembles are responsible for the activation [18].

A third mechanism was formulated originally in a form described as a metal to metal ligand effect. This is an electronic effect by which a metal adds (or could remove) electron density to (from) an adjacent metal at the reaction site to enhance its ability to chemisorb small molecules and transform them into products (see Fig. 1(c)) [19]. Recent studies of bimetallic thin films have provided evidence for the importance of such effects but have also shown that the concept is far more complex than conceived originally. Charge transfer, orbital rehybridization, modification of valence states, etc. of the metals can all play an important role in the chemisorption of small molecules (e.g. CO, ethylene etc.) on bimetallic thin films [12].

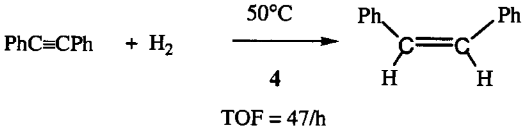
2. Catalysis by segregated platinum–ruthenium cluster complexes

We have shown recently that compound **1** can be transformed into the alkyne complex $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)_2$ (**4**) where the PhC_2Ph ligand has assumed a triply bridging position on one of the two Ru_3 triangles [3]. Most interestingly, we have found that **4** is an effective catalyst both for the hydrogenation of diarylalkynes to *Z*-diarylolefins, Eq. (1) [20], and for hydrosilylation of diarylalkynes to *E*-diaryl(silyl)olefins, Eq. (2) [21]. The turnover frequency (moles of product/mole of catalyst – h, TOF) for the formation of *Z*-stil-

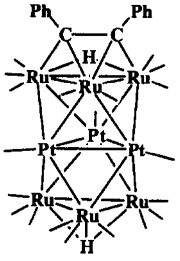


Scheme 1.

bene, 47 at 50°C, is the highest rate yet reported under these conditions for a cluster based catalysts.



(1)



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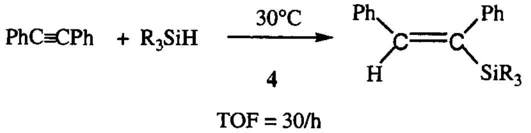
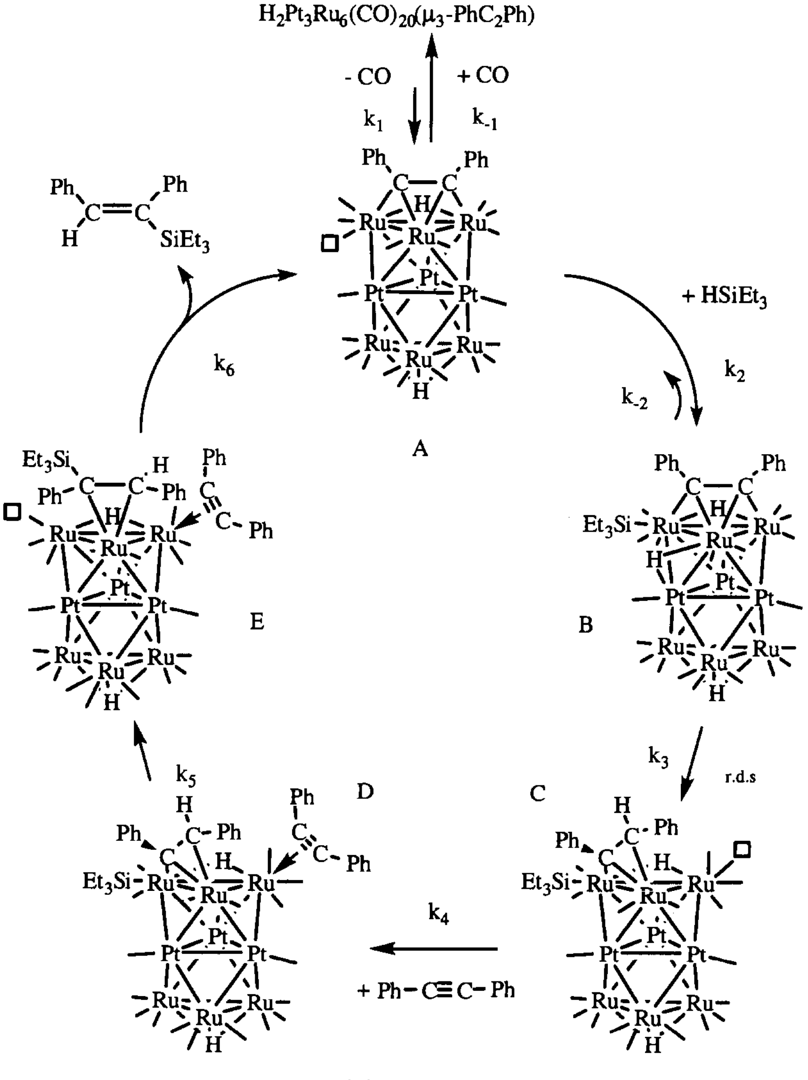
An extensive investigation of the catalysis by kinetics and substrate labeling has led to the mechanism shown in Scheme 1.



(2)

The catalyst is activated spontaneously by the dissociation of one CO ligand from the cluster to produce a vacant site for the activation of the reagents. Ligand substitution studies have shown that the most labile ligands are the ones on the ruthenium atoms that contain the alkyne ligand [22]. Assuming CO dissociation at this triruthenium group, the unsaturated intermediate **A** would be formed. The next step is believed to be the addition of hydrogen to the cluster. This probably occurs at the ruthenium atoms, but since the hydride ligands are mobile, they can readily move to the coordination sites that are thermodynamically the most stable, e.g. **B**. Studies have shown that bridging sites are the most stable forms for hydride ligands in metal cluster complexes. Next, alkyne addition to the cluster in the rate-determining step induces a sequential



Scheme 2.

transfer of two of the hydride ligands to the alkyne ligand that was coordinated to the cluster originally. The *cis* stereochemistry is established with the transfer of the first hydride ligand [1e]. The product *cis*-stilbene is eliminated and the catalytic cycle is closed.

The catalytic hydrosilylation of diphenylacetylene by **4** is believed to proceed by a similar mechanism (see Scheme 2). In this case it was established that the silane activation step precedes the alkyne addition step since the rate of the catalytic reaction is dependent on the concentration of silane, but independent of the concentration of alkyne. That is, the rate-determining step k_3 comes after the silane addition, but before alkyne addition. The rate-determining step k_3 may involve a spontaneous transfer of a hydride ligand to the alkyne. In support of this, a small deuterium isotope effect $k_H/k_D = 1.2$ was observed for this reaction.

At this time we have no evidence for the direct participation of the platinum in the transformations in either of the reactions catalyzed by **4**. Nevertheless, this catalyst is still far more active than related homonuclear clusters for these reactions. We believe that the platinum is responsible for this higher activity. It may be that the activity enhancement by platinum is as simple as an electron density donation ligand effect (see Fig. 1(c)). Increases in electron density on the ruthenium atoms should facilitate oxidative addition reactions such as the addition of hydrogen or silane at the ruthenium atoms. Further studies will be necessary to provide further confirmation of the details of the role of the platinum in the catalytic reactions of compound **4**.

The fundamental challenges remaining to further development of the catalytic properties of segregated bimetallic catalysts are: (1) synthesis of complexes that do not fragment under the conditions of catalysis; (2) being able to deposit them on to supports without extensive transformations; and (3) being able to characterize the supported clusters. Recent studies of the deposition of bimetallics on mesoporous supports have shown some very promising catalytic properties [10a,b]. The introduction of the clusters into the cavities of the mesoporous supports seems to control their size and composition while high catalytic activity is retained.

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